



SYNTHESIS AND CHARACTERIZATION OF COPPER NANO PARTICLES: APPLICATION, IN FIELD OF OXIDATION OF AROMATIC HYDROCARBONS CERIUM (IV) SULPHATE UNDER MICROWAVE IRRADIATION

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Abstract

The catalytic oxidation with Cerium (IV) in aqueous solution offers an economic and environmentally safe alternative for oxidation reactions performed in synthetic laboratories and chemical industry. In this paper we have shown that the size of the copper nanoparticle is responsible for the yield of chemical change. The copper catalyst (non-nano) powder showed 21% conversion of naphthalene to α -naphthol in 3 min under our experimental conditions. Same quantity of copper nanoparticles (size, ~ 60 nm diameter) ready by turn PVP-EG capping showed 33% conversion of naphthalene to α -naphthol that inflated to concerning 43% when 8 nm diameter capped copper nanoparticles are used. Surprisingly, 5 nm size copper nanoparticles showed no change in the yield of about 41%. [Ce(IV)-Cu(II)sulphate] system in our experimental work shows 43%, 97%, and 96% yields for oxidation of naphthalene, phenanthrene, and anthracene respectively in the presence of copper nanoparticles.

Keywords: Aromatic hydrocarbons, Cerium (IV), copper nanoparticles, PVP-EG capping, surface area.

INTRODUCTION

Research in nanoscience and nanomaterials has achieved considerable attention because of their unique properties and various applications in different areas [1-2]. Applications of such materials in different areas depend on the type and nature of nanoparticles (NPs). In moulding heterogeneous catalysts, the action between active metal species and a capping agent as a support is a promising methodology for providing unique and highly active catalysis. Now days, metallic nanoparticles are of great interest because of their excellent catalytic properties [3]. Among the metal nanoparticles, CuNPs have received considerable researcher's interest, which may be due to their best optical, electrical and thermal properties. Cu NPs were assumed cost-effective as compared to other noble metals like Ag, Au, and Pt. Thus, they are potentially applied in the field of catalysis [4]. Amongst many metals like Gold, Silver, Palladium, Platinum, towards which research is directed, copper and copper based compounds are the most important materials in the field of catalysis.

The reactivity of copper nanoparticles are due to their high surface-to-volume ratio and thus they can easily interact with other particles[5] and increase their catalytic efficiency although various physical and chemical methods have been extensively used to produce nanocrystalline copper catalyst of desired size and shape. Most of the artificial ways either yielded particles of irregular form with wide size distribution and needed warmth and pressure condition or created particles with reduced chemical reaction activity and inability to employ the particles. Little work has been distributed on the cold synthesis of copper nanoparticles [6] visible of the on top of limitations, we performed the synthesis of size-controlled copper nanoparticles catalyst through an easy one-phase binary compound route using as PVP-EG capping agent and used these nanoparticles as catalyst along with cheap oxidizer cerium (IV) sulphate for catalytic-oxidation of some hydrocarbons during this paper.

Chemistry of cerium is a very broad area which has received considerable attention through the years, resulting in substantial advance both in the synthetic [7-8] and mechanistic categories. Cerium (IV) oxidation of aromatic compounds in the presence and absence of metal ions has been frequently reported from the synthetic point of view[9]. Cerium (IV) is a well known oxidant in acidic media [10-12] having reduction potential [13-14] of the couple Ce(IV)/Ce(III)1.70V and is stable only in high acid concentration. The metal ion oxidants have been widely employed in the synthetic chemistry [15-17] including carbohydrates chemistry [18-19]. These are stable, in expensive and can readily be stored and handled.

Thabaj et al., reported the reaction of Ce (IV) oxidation of L-serine catalyzed by a small amount of Ag⁺ in aqueous sulfuric acid medium. In sulfuric acid and sulfate media, several sulfate complexes of Ce(IV) form exist such as Ce(SO₄)₄²⁺, Ce(SO₄)₃, Ce(SO₄)₂HSO₄⁻, and H₃Ce(SO₄)₄, but their role has not received much attention so far, because of the increase in the rate of reaction with increasing sulfuric acid concentration. The mechanism may be quite complicated due to the formation of different Ce (IV) complexes in the form of active species. Hence, to overcome this complication, Cu (II)-catalyzed oxidation of naphthalene by Ce (IV) has been investigated in order to understand the behavior of active species of oxidant in acid media and a suitable mechanism is proposed.

In this paper, we've reported the synthesis of CuNPs catalyst by reducing the copper ions with metal borohydride and PVP-EG as capping agent. We've varied the particle size by varying the concentrations of reactants and capping agent. The catalytic activities of these particles of different sizes have been tested on the yield of production of naphthalene to α -naphthol, anthracene to anthraquinone, and phenanthrene to 9-Fluorenone using Ce (IV) in acidic media.

Copper nanoparticles and its catalytic activities

The success of transition metal nanoparticle catalysts is due to the high surface-to-volume ratio and a high surface energy^[20]. From these properties, transition metal catalysts are being used in a variety of different reactions and mechanisms to further study their reactions and capabilities. Nanoparticles are described as being a group of particles ranging from tens to a few hundred atoms, varying in size from several tens to several hundreds of nanometers^[21]. Metal nanoparticles have been tested experimentally to display high catalytic properties in reactions for hydrogenation, hydroformylation, carbonylation^[22], cycloadditions, and numerous other reactions and mechanisms^[20]. Since nanoparticles are so small, the forces between the atoms tend to make an attraction with capping agent (PVP-EG), which causes atoms to form into larger particles, which inhibits the catalytic affect of the metal nanoparticles because of the high reactivity between particles. This attraction is because of the primary nuclei which are the most active regions of the catalyst. To offset this interaction, ligands, polymers, oxides, and other molecules are used as stabilizers for the catalyst. The substituent added to the catalyst ensures proper reaction and protect the reaction surface^[21]. This stability also plays a role in the recycling abilities of the catalyst when reacted in a colloid environment^[22]. The nanoparticles act as electron relay centers. Nucleophiles can donate their electrons to the metal particles, while simultaneously an electrophile would capture the electron and desorbs from the metal nanoparticle^[22] because the metal nanoparticle is already stabilized via capping agent or other substituent, it allows the reaction to proceed while still maintaining its stability. It is important to affix the metal nanoparticle to a suitable delivery medium^[20]. By affixing these particles, it will ensure proper reacting with the catalyst and the reaction^[21].

Transition metal ions of Ag, V, Fe, Ru and Mn etc. are reported to act as catalyst for some of the α – amino acid oxidations^[23-27]. With the emergence of metal nanoparticles possessing appreciable stability and high surface area per particle, their potential to use as catalyst for organic biochemical relevant reactions stands well documented in recent years^[28-29]. The polymer stabilized mono metal nanoparticles of cheap, cost effective and abundant transition metals like Copper when used as catalyst are expected to produce ecofriendly process enroots^[30-34]. Current literary shows that the applying of Cu-nanoparticles as catalysts in organic synthesis has been very little explored. Copper nanoparticles are notably engaging, being low-cost (they may be ready from CuSO₄), are high yielding, want mild reaction conditions and are reusable.^[35-36] Recently Rothenberg and co-workers have reported the use of copper nanoparticles, which are considerably less harmful to the environment than any other metals in Suzuki cross coupling reactions^[37]. Here in, we report a novel protocol that employs Copper nanoparticles as an efficient and selective catalyst in the oxidation of various hydrocarbons.

EXPERIMENTAL

Method and materials

Copper sulphate pentahydrate, Sodium borohydride, Trisodium citrate, Cerium(IV) sulphate, Naphthalene (E. Merck), Anthracene (Loba Chemie Industrial Co.), and Phenanthrene (E. Merck) were used as such without further purification.

Synthesis of copper nanoparticles catalyst

Copper nanoparticle catalysts were prepared in aqueous solution by reducing Cu²⁺ ions with sodium borohydride. The metallic copper ion thus produced was immediately capped by poly (N-vinylpyrrolidone) to prevent further growth. The detailed synthetic procedure of copper nanoparticles was as follows, The Cu nanoparticles were prepared in aqueous phase by chemical reduction of cupric salt solution using sodium borohydride in the presence of PVP-EG which act as a capping agent. In a typical experiment, under nitrogen atmosphere, 10 ml CuSO₄ solution (0.1 M) was magnetically stirred for 15 min and a certain amount of poly (N-vinylpyrrolidone) (PVP, MW = 55,000), acting as the capping molecule, was dissolved in ethylene glycol (EG) was added and allowed to stir for 30 min followed by adjusting the solution pH up to 11 with drop wise addition of 1 M NaOH- EG solution. 3ml of aqueous solution of sodium borohydride (0.5M) was then added drop wise to the above solution under constant stirring on magnetic stirrer. The appearance of dark reddish brown colour solution indicated the formation of PVP protected copper nanoparticle catalyst. The particles were then, extracted by ultracentrifugation of resultant solution at 30,000 rpm for 45 mins. The pelleted nanoparticles were washed repeatedly with cold water to remove any trace of free PVP-EG.

General procedure for the one-pot oxidation of aromatic hydrocarbons

In a typical procedure, cerium (IV) sulphate was taken in 500ml beaker, added 1:1 mixture of sulphuric acid and water, then stirred magnetically with frequent addition of water with gentle warming, until the salt dissolved and standardized with a standard solution of ferrous ammonium sulphate using ferroin (CDH) as an external indicator.

All other chemicals used were pure substances. A CEM Discover Microwave synthesizer was used for studying the reactions under microwave irradiation, in which control of temperature, time and power was possible. In order to achieve the maximum yield, five to seven sets were performed by changing the concentration, time temperature and other conditions of each component, which can affect the yield, for example in the synthesis of α -naphthol from naphthalene, for performing the reactions in the solution phase, 0.83 mmol of copper(II) sulphate with 4.0 mmol cerium(IV) sulphate were added to 3.4 mmol of acetic acid solution containing 1.0 mmol of naphthalene and the mixture was heated under microwave irradiation for 3 min taken in a microwave vessel. The microwave vessel was kept under microwave synthesizer at a fixed temperature for the 3 min. Contents were cooled and extracted with appropriate solvents. The extract was dried over anhydrous MgSO_4 . Solvent was removed under reduced pressure; again replacing the copper (II) sulphate solution by copper nanoparticles of different size was heated under microwave irradiation for 3 mins. Contents were cooled and extracted with chloroform. The extract was dried over anhydrous MgSO_4 . Solvent was removed under reduced pressure, and then noted the achieved yield. IR (in KBr; Brucker Vector-22 IR spectrophotometer) and ^1H NMR (Xeol 400MHz in CDCl_3 with TMS as internal standard) spectra were recorded, and reactions were monitored with thin-layer chromatography, TLC (Merck GF254 silica-gel-coated plates). TLC, IR, NMR spectra and melting points of the derivative confirmed the purity and identification of products.

RESULTS AND DISCUSSION

For a better visual understanding, the flow chart of color changes during the synthesis of copper nanoparticle, which shows that the reduction proceeds through $\text{Cu(II)} \rightarrow \text{Cu(I)} \rightarrow \text{Cu(0)}$.

During synthesis, the drop wise addition of NaOH-EG gives the pale blue CuSO_4 -EG solution result came about at first in the development of a pale blue encourage attributable prone to Cu(OH)_2 . At that point, this development step by step turned to a profound clear blue result with further addition of NaOH-EG to arrive at pH 11, as clearly showed by the critical blue shift of 214 nm in retention top of the important results. In acknowledging that hydroxide particles and ethylene glycol may facilitate with copper particles, we accept that a moderate Cu(II)-hydroxyl-EG complex may form at this stage before it is diminished by NaBH_4 . Excess of NaBH_4 -EG result initially turned the profound blue response for an almost lackluster one, and in the long run to a dark reddish brown shade. The above colorless solution result could be demonstrated that we accept that Cu(I) species is framed at this stage, since the d-d transitions might be forbidden because of a full electronic structure in the 3d orbital of Cu(I) species. The ultimate reddish brown colour formed.

Table 1: Effect of change of concentration of sodium borohydride added on the colour of copper nanoparticle

Conc. of added NaBH_4 soln. (ml)	Conc. of added capping agent (ml)	Colour of Cu nanoparticles
0.5	0.5	Pale yellow
1.0	0.5	Yellowish orange
1.5	0.5	Reddish orange
2	0.5	Reddish brown
2.5	0.5	Reddish black

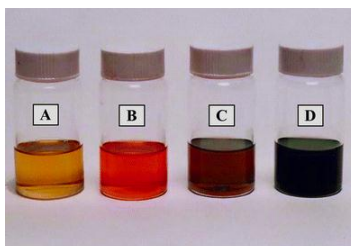


Figure 1: Colour change in Cu nano particles in base of Table 1

Characterization of copper Nano particles

UV visible spectra

Colloidal dispersion of metal particles exhibits absorption spectra in the UV–Vis region. Absorption in metal particles is mainly caused by the excitation of SPR. SPR is due to the collective oscillation of free electrons of the metal nanoparticles in resonance with the frequency of incident light wave. Nanosized Cu nanoparticles with size larger than 20 nm typically exhibit a SPR peak at 560 nm (Samim M et al). Fig. 4 represents the UV–Vis spectra of Cu nanoparticles synthesized using 0.1 M PVP-EG in the present work. In these cases a broad absorption peak in the UV–Vis spectra is obtained at 297.5 nm. As in these cases, the UV–Vis spectrum obtained at wavelength lower than 300 nm, indicating that the size of the copper nanoparticles synthesized in the present work is less than 50 nm. A broad peak around 300 nm in the UV–Vis spectra also suggests that the size of the majority of the Cu nanoparticles is uniform and varied in the small range of 20–50 nm.

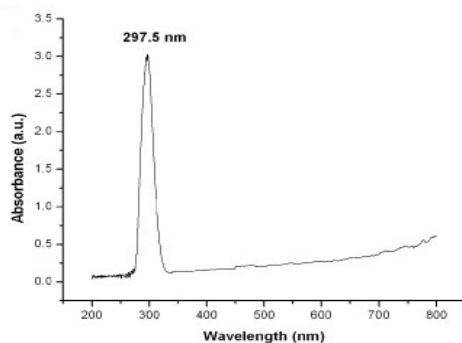


Figure 2: UV-VIS spectra of Cu/PVP-EG nanoparticles

XRD measurement

Powder X-ray diffraction measurements were performed on a Bruker AXS D8 diffractometer using pressed pellets as samples with $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$ shown in Fig1. Powder diffraction analysis indicated that the product was copper nanoparticles, the crystallite sizes of the particles were determined from the XRD spectrum using the scherrer equation. The peaks are broad due to the nano-size effect. The average crystallite size of CuO nanoparticles is found to be 10 nm using scherrer formulas.

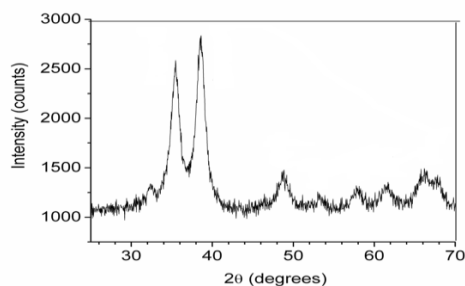


Figure 3: Powder XRD plot of copper nanoparticles prepared by [PVP-EG] system

TEM

The size of copper nanoparticle was determined by transmission electron microscopy (TEM) using a JEOL Model JEM 2000E \times 200 electron microscope. Samples were prepared by putting small drops of dispersed particles in water on coated copper grids and allowing the solvent to slowly evaporate at room temperature.

A representative TEM images of different sizes copper nanoparticles (Fig 2) and size distribution of CuNPs synthesized at varying concentrations of added cupric ion (0.0125–0.140 M) and 0.5 M concentration of added EG ions. It has been noted that without broadening the polydispersity range, on increasing the concentration of cupric ion, size of particles also increases. This result implies that controlling the concentration of constituent chemicals can control the size of nanoparticles in aqueous medium.

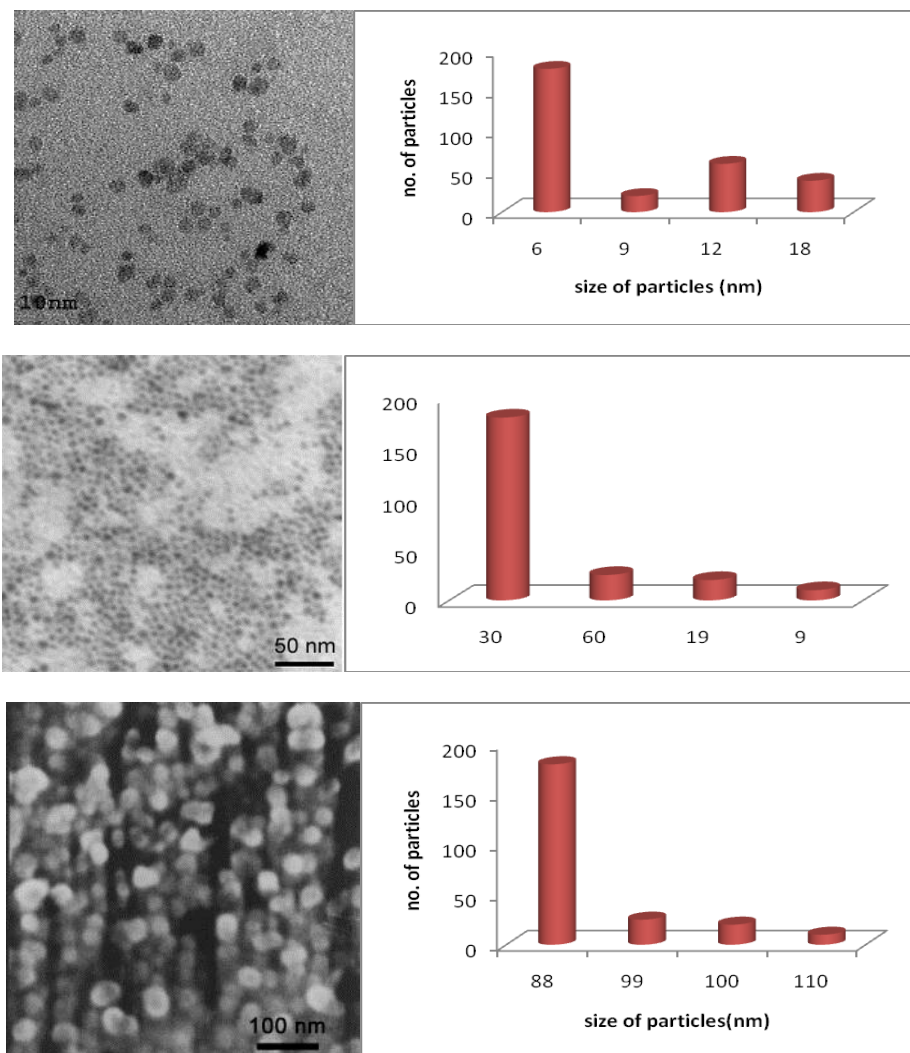


Figure 4: TEM images and Histogram of copper nanoparticles with 0.5M PVP-EG concentration and different copper ion concentrations

SEM

The morphology of the product was examined by SEM. Fig.3 depicts the SEM image of nanoparticles. It shows that the Copper nanoparticles are flower shaped. The size of particle observed in SEM image is about 75nm.

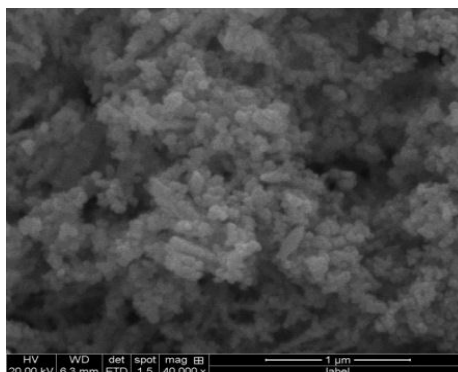


Figure 5: SEM image of the Cu/PVP nanoparticle

Table 2: Effect of the change of concentration of capping agent after immediate extraction by Centrifugation

Conc. of added $\text{CuSO}_4(\text{M})$	Conc. of added capping agent (M)	Size of the particles (nm)
0.0125	0.5	>5
0.0125	0.4	7-10
0.0125	0.3	9-12
0.0125	0.2	12-15
0.0125	0.1	<15

Table- 3: Effect of change of concentration of cupric ion added on the size of copper nanoparticles

Conc. of added Cu ion (M)	Conc. of added capping agent (M)	Size of Cu nanoparticles (nm)
0.140	0.5	80-100
0.115	0.5	55-75
0.090	0.5	40-50
0.075	0.5	30-35
0.050	0.5	10
0.025	0.5	8-6
0.0125	0.5	>5

In Table 2 it has been shown that on increasing the concentration of PVP-EG system, the particle size decreases. Using 15 ml of 0.1 M Cu (II) sulphate in the experimental procedure, the average particle size was found to decrease from 15 nm diameters to 7 nm diameters when the added PVP-EG ion concentration was increased from 0.2–0.5 M. The variation in colour of copper nanoparticle has been observed while changing the concentration of the NaBH_4 (table- 1). The change in concentration of cupric ion also had an impact on the size of nanoparticles. It was observed that the particles size increased with increase in concentration of cupric ions (table- 3).

Oxidation of hydrocarbons

A limitation of cerium (IV) oxidation in acidic conditions is usually involved therefore, it is not recommended to subject of acid sensitive compounds to such oxidation. The necessity of employing polar solvents also tends to restrict the versatility of the methodology. The major drawback associated with cerium(IV) oxidations concerns, however, the large amount of reagent required, to overcome of this problem, we introduce catalytic-oxidation process, which consumes very little amount of reagents during reaction.

We have reported the oxidation of aromatic hydrocarbons (Naphthalene, Anthracene, and Phenanthrene) with cerium(IV) results in their corresponding conversion to α -naphthol 9, 10-anthraquinone and 9-fluorenone.

Synthesis of α -naphthol was performed by the oxidation of naphthalene with cerium(IV) sulphate in the presence of copper(II) sulphate in solution phase acetic acid was used as a solvent.

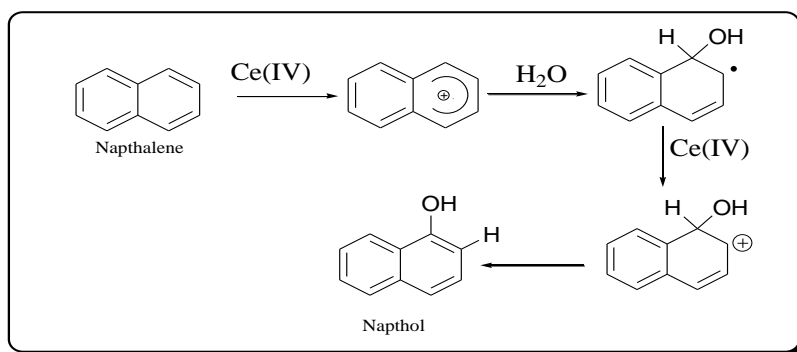


Figure 6: Mechanisms: Naphthalene converted to α -naphthol

Likewise anthracene and phenanthrene also be oxidized using cerium(IV)-copper(II)sulphate system and effect of variation of copper(II) sulphate, cerium(IV)sulphate, time and temperature has been reported by us. In all the cases, running TLC plates with the authentic sample showed only one spot. All products are known compounds and were characterized by comparison of mp and spectral data are given below.

α -naphthol (a') from naphthalene (a).

IR Peaks: ν_{\max} = 3053.64 cm^{-1} (ν OH), 1631 cm^{-1} (ν C=C), 1373 cm^{-1} (ν C-O phenolic strs), 1513 to 1584 cm^{-1} (benzenes ring str)

NMR signals: δ 7.755 - 8.007, (7h, m), δ 7.1 (1hb, s).

9, 10-Anthraquinone (b') from anthracene (b).

IR Peaks: ν_{\max} 1673.81 cm^{-1} (ν_{quinone}), 935–809 cm^{-1} ($\nu_{\text{subs. benzene ring}}$),

NMR: δ 7.05 to 8.22 (8Hm).

9-Fluorenone (c') from phenanthrene (c).

IR ν_{\max} 3054 cm^{-1} ($\nu_{\text{ArC-H}}$), 1671 cm^{-1} (ν C=O), 1600 ($\nu_{\text{C=C str}}$) and 733 cm^{-1} ($\nu_{\text{subs. benzene ring}}$).

NMR: δ 7.40 to 8.70 (8Hm).

Table 4: Effect of various factors on yield in the formation of α -naphthol from naphthalene (1.0 m mol) in the absence of Cu-nanoparticles

Entry nos.	Ce(IV)sulphate (m.mol.)	Cu(II)sulphate solution (m.mol.)	Acetic acid (m.mol.)	Naphthalene (m.mol.)	Temperature (0C)	Time (sec)	% yield (α -naphthol)
1	4.0	0.20	3.4	1.0	80	180	11.34
2	4.0	0.41	3.4	1.0	80	180	13.87
3	4.0	0.62	3.4	1.0	80	180	17.74
4	4.0	0.83	3.4	1.0	80	180	24.68
5	4.0	1.04	3.4	1.0	80	180	20.6

Table 5: Oxidation of organic substrates (dissolved in acetic acid) by cerium (IV) sulphate in presence of copper (II) sulphate in solution phase and under microwave irradiation in the presence of acetic acid, amounts of organic substrate in

Organic Substrate	Product	Acetic acid (m mol)	Ce (IV) sulphate (mmol.)	Cu(II) sulphate	MW (%) power)	Time (sec.)	M.P. (reported) oC	% Yield
Naphthalene (a)	α – naphthol (a')	3.4	6.0	0.83	80	180	92 °C (94°C).	13.87 a 24.68b 25.2c 30.25d
Anthracene (b)	Anthraquinone (b')	3.4	4.0	0.61	60	180	282 oC (286oC).	77.0a 93.5b 94.01 c 97.1d.
Phenanthrene (c)	9-Fluorenone (c')	3.4	4.0	0.45	80	180	82 oC (85oC).	71.4a 83.4b 90.1 c 97.4 d

a: In the absence of catalyst.

b: In the presence of copper soln catalyst.

c: In the presence of copper nano catalyst(uncapped).

d: In the presence of capped nano catalyst.

All the cases substrate is 1.0 mmol.

The total yields of anthraquinone and 9-Fluorenone in the oxidation of anthracene and phenanthrene respectively for different copper powders are summarized in table 6. The particle size of different copper powders was included in the table for comparison. The uncapped and undefined macro sized copper powder showed 24% conversion of naphthalene to α -naphthol in 3 min under our experimental conditions. Same quantity of copper nanoparticles (size, ~ 60 nm diameter) ready by turn PVP-EG capping showed 25% conversion of naphthalene to α -naphthol that inflated to concerning 28% when 8 nm diameter capped copper nanoparticles are used. Surprisingly, 5 nm size copper nanoparticles showed no change in the yield of about 30.2%. [Ce (IV)-Cu (II) sulphate] system .

The higher catalytic activity towards the oxidation of naphthalene could be due to the higher catalytic surface area of small nanoparticles. It is presumed that the electrophilic nature of the catalyst surface renders a weak bond between the π -system of aromatic ring and vacant d-system of copper atoms, which gives slightly positive charge over the ring. The whole complex reacts with another molecule of naphthalene to produce α -naphthol. The electrophilic nature of copper surface obviates that when the particles are extremely small in size, the electrons are pumped into copper by the benzene π -system, which usually reduces the band gap between Fermi level and conduction band considerably so that the catalytic activity is also expected to be reduced (Huynh et al 2003). However, copper has d-bands well below the Fermi level and the antibonding stage at the top of the d-bands end up below the Fermi level and are filled (Sharma et al 2003; Nilsson et al 2005). As a result, the catalytic activity did not decrease rather it remained constant. Any aggregation of the particles in aqueous dispersion leads to lower efficiency. The freshly prepared and capped Cu nanoparticles also showed good activity for oxidation.

Table 6: Dependence of yield of anthracene, naphthalene and phenanthrene (%) on size of the copper nanoparticles

Particles size (nm)	Approximate yield (%) Anthraquinone	Approximate yield (%) α - naphthol	Approximate yield (%) 9-Fluorenone
85-95	85.15	22.4	89.2
60-70	88.45	24.8	90.8
30-40	90.2	25.7	93.5
5-10	95	28.1	94.7
Less than 5	97.1	30.2	97.4

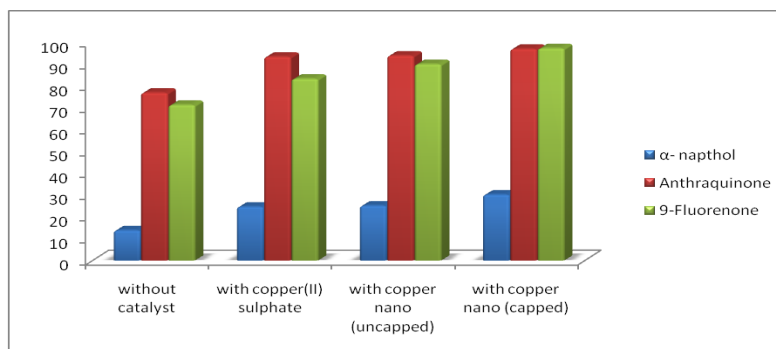


Figure 7: Comparison of the maximum yield different of the naphthalene, anthracene and phenanthrene in the absence of catalyst, in the presence of copper (solution) catalyst, in the presence of copper nano catalyst (uncapped), in the presence of capped nano catalyst

CONCLUSIONS

In the present study the strong oxidizing power of cerium (IV) has been shown to be further enhanced by the use of traces of copper (II) sulphate and copper nanoparticles. It may be mentioned that catalyzed oxidation of organic compounds by cerium(IV) from the synthetic point of view has not been reported with copper nanoparticles, which is one of the cheapest and most easily available catalyst. To the best of our knowledge, with the present system higher yields have been obtained compared to the other methods reported so far. In the present work a new field in the form of cerium (IV) – copper (II) sulphate system has been explored for the oxidation of various organic compounds from the synthetic point of view. In this paper, we have described a new synthetic route of preparing CuNPs in aqueous solution using sodium borohydride at room temperature and coated with a weak adsorbing agent like PVP-EG on the particle surface which controls the particle size. We have also discussed the yield comparison using copper (II) sulphate solution and CuNPs respectively. The catalytic efficiency increases up to certain minimum particles size, below which it remains constant. The method is, however, cost effective and scaling up is possible.

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